

**Promotion of Intermolecular
Monoelectronic Reactions
in the Electrocatalytic Reduction
of Alkyl and Glycosyl Halides on Silver:
an Efficient Way to Coupling Reactions**

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The electroreduction of organic halides on silver, which was the object of our study in the last years¹⁻¹⁰, provides a remarkable example of organic electrocatalytic process, and fosters very interesting fundamental and applicative developments. In fact, on one side this process, involving three actors, namely $R\cdots X\cdots Ag$, is a most appropriate model subject for the development of interpretative schemes in organic electrocatalysis, since any such scheme would necessarily require to take into account the specific interactions between the metal and the reacting surface¹⁰, and the halogen specific adsorption onto silver has been a favourite topic of many important schools; on the other side, many applicative advantages can be expected from the following two major features of the electrocatalytic performance of silver:

(a) the remarkable shift in positive direction (0.4–1.1V in acetonitrile/tetraethylammonium perchlorate, according to the halide structure) of the reduction potentials of all organic halides (about fifty compounds tested so far, including alkyl, glycosyl, benzyl and aryl ones), affords a much wider range of candidates for direct electroreductions, together with higher selectivities and lower energy consumptions;

(b) in the cases of alkyl and glycosyl halides, a remarkable promotion of intermolecular monoelectronic reactions with respect to the bielectronic intramolecular ones, which we have justified with the presence of an attenuated radical $R\cdots X\cdots Ag$ and a “cage effect” provided by the silver surface^{6,8,10}, mainly observed with glycosyl halides. This effect affords coupling reactions between coadsorbed species leading to dimers and adducts, sometimes unexpected and difficult to synthesize otherwise²⁻⁸, and is especially attractive from a synthetic point of view.

A rich selection of examples will be provided and discussed, especially focusing on the effects of the molecular structure and of the operating conditions on the product distribution.

Dimerizations

Under proper conditions, electroreduction of glycosyl halides on silver affords almost quantitatively C-C-glycosyl dimers, while electroreduction of alkyl halides, such as haloadamantanes, affords dimers in competition with the hydrogenation product, very probably as a consequence of a lowering of the free electrocatalytic surface induced by product filming. For both cases examples of mixed dimerizations will be also provided and discussed.

Coupling with or addition to acceptors

Electroreduction of glycosyl halides in the presence of acceptors coadsorbed within the “cage” afforded

formation of C-alkyl- (with α,β unsaturated nitriles as acceptors, the products being selectively in α configuration) and O-aryl-glycosides (with phenols as acceptors, the products being in α and/or β configuration according to the operating conditions)

Electroreduction of glycosyl halides and alkyl halides in the presence of alcohols results in ether formation (together with other products).

Cyclizations

A preliminary investigation will be discussed on two model compounds, namely 2,2'-bis(bromomethyl)-1,1'-biphenyl and 1,10-dibromodecane, as model compounds for favoured and unfavoured cyclization, respectively.

In conclusion, silver cathodes, having unique properties, can be regarded as a valuable tool for organic halide reductions. They actually show the best electrocatalytic activity among the cathode materials so far tested for this reaction, an activity which can be modulated by an appropriate choice of the operating conditions. Moreover, in the case of alkyl and glycosyl halides, electroreductions on silver can be regarded as a source of attenuated radical intermediates in high local concentration (the “cage effect”), thus appearing as an interesting, alternative synthetic methodology.

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